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(54) Hydantoin compounds

Hydantoinverbindungen

Composés d'hydantoine

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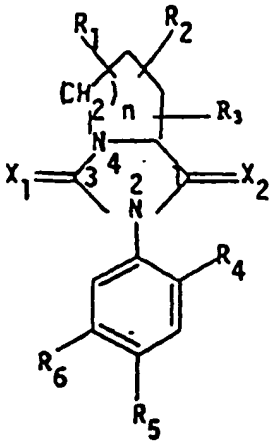
Description

This invention relates to novel 2-(2,4,5-substituted phenyl) hydantoin compounds, intermediates therefor, synthesis thereof, and the use of said compounds for combatting weeds.

More particularly, one aspect of this invention relates to compounds of the formula (I)



(I)

wherein

R_1 is H, C_{1-4}alkyl, C_{2-4}alkenyl or halo;

R_2 is H or halo;

R_3 is halo;

R_4 is H or halo;

R_5 is halo, cyano or C_{1-4}alkyl;

R_6 is halo; NO_2; NH_2; CN; C_{2-8}alkynyl; C_{2-8}alkenyloxy, C_{2-8}alkynyloxy, $O(C_{1-4}alkylene)_kR_7$, or $S(C_{1-4}$ alkylene$)_kR_7$, each of which is optionally substituted by CN or one or more halo; C_{1-8}alkyl optionally substituted with one or more groups selected from halo and CN; C_{2-8}alkenyl optionally substituted by one or more halo; C_{2-5}alkoxy carbonylC_{1-4}alkyl, whereby the carbon atom of the alkyl group alpha to the alkoxycarbonyl group may be substituted with one more C_{2-5}alkoxycarbonyl group or a cyano group; C_{2-5}alkoxycarbonyloxy; C_{2-5}alkoxycarbonylC_{1-4}alkoxyC_{1-4}-alkyl; alkyl; C_{2-5}alkoxycarbonylC_{2-5}alkenyl, whereby the alkenyl group is optionally substituted by halogen; C_{1-4}alkylthio-C_{1-4}alkyl; C_{1-4}alkylsulfonylC_{1-4}alkyl; C_{1-4}alkylsulfonyl; C_{1-4}alkylsulfonyloxy; C_{1-4}alkoxyC_{1-4}alkoxy; $OCH(SR_8)COOR_9$; $NR_{10}R_{11}$; $COOR_{12}$; $C(O)NR_{13}R_{13}'$; $C(O)R_{14}$; R_{15}; $CR_{14}(OC_{1-2}alkyl)_2$ or $CR_{14}(SC_{1-2}alkyl)_2$ whereby the alkyl groups optionally join together to form a ring; $CR_{14}=NOR_{13}$; thienylC_{1-4}alkoxy wherein the thienyl is optionally halo substituted; or C_{1-4}alkoxyC_{1-4}alkoxycarbonyl;

or R_5 and R_6 join together with the phenyl ring to form a bicyclic ring containing nine to ten ring atoms, one to three of said ring atoms optionally being selected from oxygen, nitrogen and sulfur, and optionally being substituted with one or more groups selected from C_{2-8}alkynyl, halo, oxo, C_{1-4}alkylene-R_{16}, and C_{2-8}alkenyl and C_{1-8}alkyl which is itself optionally substituted by C_{2-5}alkoxycarbonyl, C_{1-4}alkoxy or CN;

R_7 is H; C_{1-4}alkyl, C_{2-5}alkenyl, C_{2-5}alkynyl, or C_{3-8}cycloalkyl, which hydrocarbyl is unsubstituted or substituted by one or more halo or by CN; cyclopentanonyl; phenyl optionally substituted by O-C_{1-4}alkylene-$COOR_8$; -$COOR_8$; C_{2-5}alkanoyl; C_{2-5}alkoxycarbonyl wherein the alkoxy is optionally substituted by

C_{1-4}alkylthio; $C(O)NR_8R_8'$; $C(=NOR_8)COOR_8'$; $P(O)(OR_8)OR_8'$; R_{15}; $C(O)R_{15}$; cyclopentoxycarbonyl; or phenoxy;

R_8 and R_8' independently are C_{1-4}alkyl;

R_9 is C_{1-4}alkyl optionally substituted by one or more halo;

R_{10} is H or C_{1-4}alkyl;

R_{11} is H; C_{1-4}alkyl, optionally substituted by $P(O)(OR_8)R_8'$; C_{2-5}alkanoyl; C_{2-5}alkoxycarbonyl; or C_{2-5}alkoxycarbonylC_{1-4}-alkyl;

R_{12} is H; C_{1-10}alkyl; phenyl; an aromatic 5- or 6-membered ring comprising 1 to 3 heteroatoms selected from oxygen, sulphur and nitrogen; $N=C_{2-8}$alkylidene; or C_{1-4}alkyl substituted by one or more groups selected from C_{1-10}alkyl, cycloalkyl, C_{2-10}alkenyl, cycloalkenyl, C_{2-10}alkynyl, $NR_{10}R_{11}$, C_{1-4}alkylthio, CN, phenyl, an aromatic 5- or 6-membered ring comprising 1 to 3 heteroatoms selected from oxygen, sulphur and nitrogen, C_{2-5}alkanoyl, halo, C_{1-4}alkoxy, tri(C_{1-4}alkyl)silyloxy, tri(C_{1-4}alkyl)silyl, C_{2-5}alkoxycarbonyl, $P(O)(OR_8)OR_8'$, C_{2-5}alkanoyloxy, and di(C_{1-4}alkyl)aminocarbonyloxy in which both alkyl groups may be tied together to form a saturated 5 to 6 membered heteroring optionally containing one further heteroatom selected from 0, S and N, and in which any further N-heteroatom present may, depending on the hydrogenation degree of the heteroring, bear a hydrogen or a C_{1-4}alkyl group;

R_{13} is H or C_{1-4}alkyl; and

R_{13}' is H, C_{1-4}alkyl, C_{1-4}alkoxy, phenyl, CHO, C_{2-5}alkanoyl, C_{1-4}alkylsulfonyl, C_{2-5}alkoxycarbonylC_{1-4}alkyl or C_{2-5}alkoxycarbonylC_{1-4}alkoxy; or

R_{13} and R_{13}' together form a 5 to 6 membered heteroring optionally containing one or two further heteroatoms selected from O, S and N, whereby, depending on the hydrogenation degree of the heteroring, any further N-heteroatom may bear hydrogen or be substituted by C_{1-4}alkyl;

R_{14} is H or C_{1-4}alkyl;

R_{15} is a heterocyclic ring having 5 or 6 ring atoms, one to three of said ring atom being selected from oxygen, sulfur and nitrogen, which ring is optionally substituted with one or more groups selected from C_{1-4}alkyl and C_{2-5}alkoxycarbonyl;

R_{16} is tetrahydropyranyl, 5,6-dihydro-2H-thiinyl, pyridyl, pyrazinyl, oxazolyl, or oxadiazolyl all of which are optionally substituted with C_{1-4}alkyl;

X_1 and X_2 are independently 0 or S;

k is 0 or 1; and

n is 1 or 2.

Any alkyl group in the compound of formula (I) may be branched or straight chain and preferably has one to four carbon atoms.

Any alkenyl or alkynyl group may be either branched or straight chain and preferably has two to five carbon atoms.

Halo as used herein, refers to Cl, F, Br or I.

Any cycloalkenyl group preferably has five to six carbon ring atoms.

Any cycloalkyl group preferably has three to five carbon ring atoms.

When R_3, R_6, R_7, R_9 or R_{12} is substituted by halogen, it is preferably chlorine or fluorine, more preferably fluorine.

Where R_5 and R_6 join together with the phenyl ring to form a bicyclic ring, it is preferably an indanone; a benzazinone, particularly a quinolinone; a benzoxazinone; a benzodiazinone, particularly dihydroquinoxalinone; a benzothiazinone; a benzodioxane; a benzopyrane; a benzopyrone, particularly coumarin; a benzazole, particularly an indole, an indolone, an indazole, a benzotriazole, an isatine or a benzimidazolone; a benzoxazolone; a benzothiazolone; a

benzofurane; or a benzdioxolane.

n is preferably 2. Where n is 2, preferably R_3 is in the 7-position.

R_6 is preferably C_{1-4}alkoxy, C_{2-5}alkenyloxy, C_{2-5}alkynyloxy, C_{2-5}haloalkenyl, C_{2-5}alkynyl or $COOR_{12}$, in which R_{12} is as defined above. Typical examples of preferred R_6 significances inlcude isopropoxy, methoxy, O-CH(CH_3)-C≡H, C≡H, $COOCH_3$, $COOCH(CH_3)_2$, $COOC(CH_3)_3$ and $COOCH(CH_2F)_2$. R_6 is more preferably C_{1-4}alkoxy.

R_1 is preferably hydrogen or halo, more preferably hydrogen.

R_2 is preferably hydrogen.

R_3 is preferably fluoro or chloro particularly fluoro.

R_4 is preferably F.

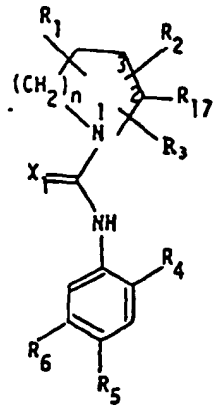
R_5 is C_{1-4}alkyl, halo or CN, particularly Cl.

Herbicidally active N-phenylhydantoines have been described in the art in e.g. EP-A-070 389, EP-A- 211 805, EP-A-272 594, EP-A-349 748, and EP-A-384 973.

A particularly preferred subgroup of compounds of the formula (I) are those in which X_2 is oxo, R_1 is H or halo, R_2 is H, R_3 is halo, R_4 is F, R_5 is Cl, CN or Br, and R_6 is C_{1-4}alkoxy, C_{2-5}alkynyl, C_{2-5}alkoxycarbonyloxy, C_{2-5}alkoxycarbonyl, C_{2-5}alkoxycarbonylC_{1-4}alkoxy, phenoxyC_{1-4}alkoxy, C_{1-4}alkoxyC_{1-4}alkoxy or C_{1-4}alkoxyC_{1-4}alkoxycarbonyl.

Compounds of the formula (I) are useful because they demonstrate herbicidal activity.

Compounds of the formula (I) can be obtained through the condensation reaction between the amide and the group R_{17} of the compound of formula (II)



(II)

wherein R_{1-6}, X_1, and n are as defined above;

R_{17} is	$C(X_2)OH$; $C(X_2)OW$; COSW; COON=CWW'; $CONHSO_2W$; $CONHOCH_2COOW$; $COOCH_2OCOW$; COOCHWOCOW'; or $CONHOCH_2COOH$; and
W and W' are	independently C_{1-8}alkyl, C_{2-8}alkenyl, C_{2-8}alkynyl, or phenyl, each of which is optionally substituted by CN, C_{1-4}alkoxy or one or more halo.

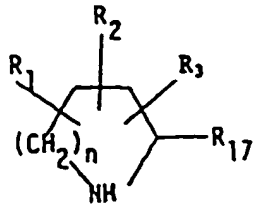
This condensation reaction is carried out under conditions that are typical for preparing hydantoin compounds. The reaction is facilitated by the presence of an acid or an alkaline agent.

In cases where n is 1, the condensation reaction is preferably carried out under acidic conditions. Accordingly, the reaction may be carried out in an inert medium such as dioxane in the presence of an acid such as HCl. Suitable temperatures range from about room to reflux temperature, the preferred temperature being reflux. The desired end-product may be obtained from solution by known techniques such as distillation, crystallization and chromatographic methods.

In cases where n is 2, the condensation reaction may be carried out under acidic or alkaline conditions. Accordingly, the reaction may be carried out in an inert medium such as toluene in the presence of an alkaline agent such as triethylamine. Suitable temperatures range from about room to 60°C, preferably about 50°C. The resulting product is isolated and purified in accordance with known processes such as extraction and crystallization.

Compounds of the formula (II) are useful not only as intermediates in the production of compounds of the formula (I), but also because they themselves demonstrate herbicidal activity. preferred groups n, and R_{1-6} are as previously mentioned. Where W and/or W' is optionally substituted C_{1-8}alkyl it has preferably 1-4 carbon atoms. Where W and/or W' is optionally substituted C_{2-8}alkenyl or C_{2-8}alkynyl it has preferably 2 to 5 carbon atoms. R_{17} is preferably COOH or $COOC_{1-4}$alkyl.

Compounds of the formula (II) may be prepared by reacting a compound of the formula (III)



(III)

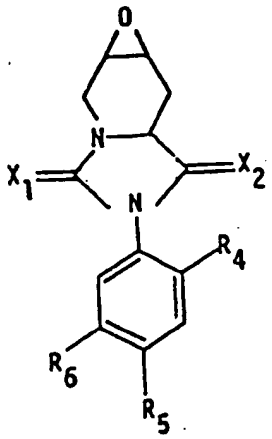
wherein R_{1-3}, R_{17} and n are previously defined with the desired substituted phenyl isocyanate or isothiocyanate. This reaction may be carried out in an inert medium such as toluene, preferably at ambient temperature. The resulting compound of formula (II) can be recovered from solution by standard separation techniques, e.g. suction filtration and chromatography.

The substituted phenyl isocyanates or isothiocyanates to be employed in the process for the preparation of the compounds of formula II are known. Compounds of the formula (III) are either known or can be prepared from known compounds according to known procedures.

Certain compounds of the formulae (I) and (II) are conveniently prepared by first preparing the corresponding compound wherein R_3 = OH followed by the appropriate exchange of R_3 substituents.

Thus, e.g., compounds of formulae (I) or (II) in which R_3 = fluoro can be prepared by treating compounds of formulae (I) or (II) in which R3 is OH with e.g. SF_4 or diethylaminosulphurtrifluoride (DAST).

Regio-isomers of the formula I wherein n is 2, R_1 and R_2 are H and R_3 is 7-F or 6-F and wherein R_{4-6}, X_1 and X_2 are as previously defined can be prepared by treating a compound of the formula IV



IV

wherein R_{4-6}, X_1 and X_2 are as previously defined with e.g. triethylamine-tris-hydrofluoride. Compounds of the formula IV are either known or obtainable from known, analogous starting materials using known procedures.

The compounds of formulae (I) and (II) are effective in controlling the growth of plants. By plants it is meant germinating seeds, merging seedlings and established vegetation including underground portions. In particular, the compounds are useful as herbicides as indicated by causing damage to both monocotyledoneous and dicotyledoneous plants in various standard evaluations for determining such effects. The herbicidal effects are exhibited both pre- and post-emergence the plants. Such herbicidal effects indicate that the compounds of formulae (I) and (II) are particularly of interest in combatting weeds (unwanted plants).

The compounds of the formulae (I) and (II) are indicated mainly to be stronger acting against dicotyledoneous plants than monocotyledoneous plants. Relatively less toxicity towards crops than towards weeds is further indicated. Hence, the compounds are of particular interest as selective herbicides to combat weeds in a crop locus, particularly at the locus of a crop such as, for example, sugarbeet, sunflower, cotton soybean, corn and wheat.

The present invention therefore also provides a method of combatting weeds in a locus which comprises applying to the weeds or their locus a herbicidally effective amount of a compound of the invention. When selective action is desired in crop locus, the amount applied will be sufficient to combat weeds without substantially damaging the crop.

For general herbicidal as well as selective herbicidal use of the compounds of the invention, the particular amounts to be applied will vary depending upon recognized factors such as the compound employed, the plants primarily in the locus, the timing, mode and formulation in application, the various conditions of treatment such as soil and weather and the like. However, in general, satisfactory results in weed control are usually obtained upon application of the compounds of the invention at a rate in the range of from 0.001 to 2 kg/hectare, more usually 0.01 to 1 kg/hectare, and preferably 0.01 to 0.25 kg/hectare, the application being repeated as necessary. When used in crops, the application usually will not exceed about 1 kg/hectare, and is usually in the range of 0.01 to 0.5 kg/hectare.

For practical use as herbicides, the compounds of formulae (I) and (II) may be and are preferably employed in herbicidal compositions comprising a herbicidal effective amount of the compound and an inert carrier which is agriculturally acceptable in the sense of not, by reason of its presence, poisoning the agricultural environment including the immediate soil of application or any crops present therein or otherwise being unsafe for application. Such compositions of formulations may contain 0.01% to 99% by weight of active ingredient, from 0 to 20% by weight of agriculturally acceptable surfactants and 1 to 99.99% by weight of the inert carrier. Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms of composition typically contain between 0.01 and 25% by weight of active ingredient, but lower or higher levels of active ingredient can, of course, be present depending on the intended use and the physical properties of the compound. Concentrate forms of composition intended to be diluted before use generally contain between 2 and 90%, preferably between 10 and 80% by weight of active ingredient.

Useful compositions or formulations of the compounds of the invention include dusts, granules, pellets, suspension concentrates, wettable powders, emulsifiable concentrates and the like. They are obtained by conventional manner, e.g. by mixing the compounds of the, invention with the inert carrier. More specifically, liquid compositions are obtained by mixing the ingredients, fine solid compositions by blending and, usually grinding, suspensions by wet milling and granules and pellets by impregnating or coating (preformed) granular carriers with the active ingredient or by agglomeration techniques.

For example, dusts can be prepared by grinding and blending the active compound with a solid inert carrier such as talc, clay, silica and the like. Granular formulations can be prepared by impregnating the compound, usually dissolved in a suitable solvent, onto and into granulated carriers such as the attapulgites or the vermiculites, usually of a particle size range of from about 0.3 to 1.5 mm. Wettable powders, which can be dispersed in water or oil to any desired concentration of the active compound, can be prepared by incorporating wetting agents into concentrated dust compositions.

Alternatively, the compounds of the invention may be used in micro-encapsulated form.

Agriculturally acceptable additives may be employed in the herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion.

Surfactant as used herein means agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersiblity or other surface-modifying properties properties. Examples of surfactants are sodium lignin sulphonate and lauryl sulphate.

Carriers as used herein mean a liquid or solid material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaeous earth, for liquid concentrate forms, a hydrocarbon such as xylene or an alcohol such as isopropanol; and for liquid application forms, e.g. water or diesel oil.

The compositions of this application can also comprise other compounds having biological activity, e.g. compounds having similar or complementary herbicidal ativity or compounds having antidotal, fungicidal or insecticidal activity.

Typical herbicidal composition, according to this invention, are illustrated by the following Examples A, B and C in which the quantities are in parts by weight.

EXAMPLE A

Preparation of a Dust

10 Parts of a compound of formulae (I) or (II) and 90 parts of powdered talc are mixed in a mechanical grinder-blender and are ground until a homogeneous, free-flowing dust of the desired particle size is obtained. This dust is suitable for direct application to the site of the weed infestation.

EXAMPLE B

Preparation of Wettable Powder

25 Parts of a compound of formulae (I) or (II) are mixed and milled with 25 parts of synthetic fine silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium ligninsulphonate and 45 parts of finely divided kaolin until the mean particle

size is about 5 micron. The resulting wettable powder is diluted with water before use to a spray liquor with the desired concentration.

EXAMPLE C

Preparation of Emulsifiable Concentrate (EC)

13 Parts of a compound of formulae (I) or (II) are mixed in a beaker with 7 parts of Toximul 360A (a mixture of anionic and non-ionic surfactants containing largely non-ionic surfctants), 24 parts of dimethylformamide and 56 parts of Tenneco 500-100 (predominantly a mixture of alkylated aromatics such as xylene and ethylbenzene) until solution is effected. The resulting EC is diluted with water for use.

FINAL COMPOUNDS

Unless otherwise indicated, temperatures herein stated are in Celsius.

EXAMPLE (intermediate)

2-[4-chloro-2-fluoro-5(isopropoxy)-phenyl]-7-hydroxy-tetrahydroimidazo[1,5a]-pyridine 1,3 (2H,5H)-dione.

545 mg (2.38 mmole) of solid, finely powdered 4-chloro-2-fluoro-5-isopropoxyphenyl isocyanate are added with stirring to a solution of 380 mg (2.38 mmole) of 4-hydroxy-2-piperidine carboxylic acid methyl ester in 10 ml of anhydrous toluene.

The reaction solution is stirred at room temperature for a period of 3 hours and is then filtered by suction. The organic solvent is evaporated. The crude product is chromatographed on a silica gel column with hexane:ethyl acetate (4:1).

The title compound is obtained as a colorless powder with a m.p. of 156-158°C.

EXAMPLE 1

2-[4-chloro-2-fluoro-5(isopropoxy)-phenyl]-7-fluoro-tetrahydroimidazo[1,5a]-pyridine 1,3 (2H,5H)-dione.

To a stirred solution of 2-[4-chloro-2-fluoro-5(isopropoxy)phenyl]-7-hydroxy-tetrahydro-imidazo[1,5a]-pyridine 1,3 (2H,5H)-dione (1 g, 2,8 mmole) in 20 ml anhydrous methylene chloride at -78°C is added in one portion 1,36 ml of diethylaminosulphurtrifluoride (DAST). The reaction mixture is brought to room-temperature and stirred for 12 hours.

The reaction mixture is evaporated and purified on a silica gel column with hexane:ethyl acetate (1:1). The desired product is obtained as a liquid (compound 1.1, Table A), Rf = 0.42 (on silica gel with hexane-ethyl acetate 1:1).

Following the procedure of Example 1, compounds 1.2-1.22 of Table A, below are synthesized.

TABLE A

Compounds of the formula (I) in which X_2 is O, R_2 is H and R_4 is F.

Compound No.	n	X_1	R_1	R_6	R_3	R_5	m.p. or Rf on silica gel
1.1	2	O	H	isopropoxy	7-F [1]	Cl	0.42 (hexane:ethyl) acetate 1:1)
1.2	1	O	H	isopropoxy	6-F	Cl	90-92°C; 0,13 (hexane:ethyl-acetate 1:1)
1.3	1	O	H	isopropoxy	7-F [4]	Cl	0.25 (hexane:ethyl-acetate 1:2)

Compound No.	n	X_1	R_1	R_3	R_5	R_6	m.p. or Rf or SiO_2
1.4	2	0	H	-7F	CN	isopropoxy	147°-149°
1.5	2	0	H	-7F	Br	isopropoxy	0,32 (Hexane:ethyl-acetate 1:1)
1.6	2	0	H	-7F	Cl	methoxy	0,18 (hexane:ethyl-acetate 1:1)
1.7	2	0	H	-7F	Cl	methoxy-carbonyloxy	0,23 (hexane:ethyl-acetate 1:1)
1.8	2	0	6-bromo	-7Br	Cl	isopropoxy	0,50 (hexane:ethyl-acetate 2:1)

Compound No.	n	X_1	R_1	R_3	R_5	R_6	m.p. or Rf or SiO_2
1.9	2	O	H	6-F	Cl	isopropoxy	0,38 (hexane: ethyl-acetate 4:6)

Compd. No.	n	X_1	R_1	R_6	R_3	R_5	m.p. or Rf on silical gel
1.10	2	O	H	isopropoxy	7-F [3]	Cl	0,30 (hexane:ethyl acetate 1:1)
1.11	2	O	H	methoxy	7-F [3]	Cl	0,18 (hexane:ethyl acetate 1:1)
1.12	2	O	H	$-O-CH(CH_3)-CH\equiv CH$	7-F	Cl	166-168°
1.13	2	O	H	$-C(O)-OCH(CH_3)_2$	7-F	Cl	0,40 (hexane:ethyl acetate 1:1)
1.14	2	O	H	$-O-CH(CH_3)-C(O)OCH_3$	7-F	Cl	0,25 (ethyl acetate; hexane 1:1)
1.15	2	O	6-Iodo	isopropoxy	7-F	Cl	0,41 (hexane; ethyl acetate 1:1)
1.16	2	O	H	$-O-(CH_2)_2-O-C_6H_5$	7-F [3]	Cl	0,24 (hexane:ethyl acetate 1:1)

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1.17	2	O	H	$-O-(CH_2)_2-O-C_6H_5$	7-F [1]	Cl	0,28 (hexane:ethyl acetate 1.1)
1.18	2	O	H	$-C(O)O-CH(CH_3)-CH_2-OCH_3$	7-F [3]	Cl	0,16 (hexane:ethyl acetate 1:1)
1.19	2	O	H	$-C(O)O-CH(CH_3)-CH_2-OCH_3$	7-F [1]	Cl	0,24 (hexane:ethyl acetate 1:1)
1.20	2	O	H	5-Cl-thien-2-yl-methoxy	7-F	Cl	
1.21	2	O	H	ethoxymethoxy	7-F	Cl	
1.22	2	O	H	$-C(O)O-CH(CH_3)_3$	7-F	Cl	0.43 (hexane:diethylether 1:1)

[1] trans with respect to the 8a position

[3] cis with respect to the 8a position

[4] trans with respect to the 7a position

INTERMEDIATES

EXAMPLE 2

1-[[(4-chloro-2-fluoro-5-isopropoxy) phenyl] aminocarbonyl](2S)-4-cis-fluoro pyrrolidine-2-carboxylic acid methyl ester

To a stirred solution of 1,27 ml (10,4 m mole) of diethylaminosulphurtrifluoride (DAST) in 20 ml anhydrous methylene chloride at -78°C is added a chilled solution of 1 g (2,6 m mole) of 1[[(4-chloro-2-fluoro-5-isopropoxy)phenyl]aminocarbonyl]-(2S)-4-trans--hydroxy-pyrrolidine-2-carboxylic acid methyl ester. The reaction mixture is stirred further for two hours at -78°C and then brought to room-temperature and stirred further for 12 hours at this temperature. The reaction mixture is evaporated and purified on a silica gel column with hexane: ethyl acetate (3:1). The desired product is obtained as a liquid having R_f = 0.13 (hexane:ethyl acetate 3:1) (Compound 2.1, Table B).

Following the procedure for Compound 2.1, Compounds 2.2-2.3 are synthesized.

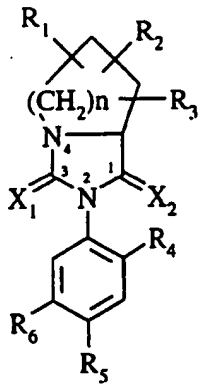
TABLE B

Compounds of the formula (II) in which R_1 and R_2 are H, R_4 is F and R_5 is Cl.						
Comp. No.	**n**	**X_1**	**R_6**	**R_3**	**R_{17}**	**m.p. or R_f on silica**
2.1	1	0	isopropoxy	4-F(4cis/2S)*	$COOCH_3$	0.13 (hexane:ethyl acetate 3:1)
2.2	1	0	isopropoxy	3-Cl(3cis)*	COOH	158-159°C
2.3	1	0	$OCH_2{\equiv}CH$	3-Cl(3cis)*	COOH	162-163°C

* the geom. configuration is with respect to group R_{17}.

Claims

1. A compound of the formula (I)



(I)

wherein

R_1 is H, C_{1-4}alkyl, C_{2-4}alkenyl or halo;

R_2 is H or halo;

R_3 is halo;

R_4 is H or halo;

R_5 is halo, cyano or C_{1-4}4alkyl;

R_6 is — halo; NO_2; N_2; CN; C_{2-8}alkynyl; C_{2-8}alkenyloxy, C_{2-8}alkynyloxy, $O(C_{1-4}alkylene)_kR_7$, or $S(C_{1-4}alkylene)_kR_7$, each of which is optionally substituted by CN or one or more halo; C_{1-8}alkyl optionally substituted with one or more groups selected from halo and CN; C_{2-8}alkenyl optionally substituted by one or more halo; C_{2-5}alkoxy carbonylC_{1-4}alkyl, whereby the carbon atom of the alkyl group alpha to the alkoxycarbonyl group may be substituted with one more C_{2-5}alkoxycarbonyl group or a cyano group; C_{2-5}alkoxycarbonyloxy; C_{2-5}alkoxycarbonylC_{1-4}alkoxyC_{1-4}-alkyl; C_{2-5}alkoxycarbonylC_{2-5}alkenyl, whereby the alkenyl group is optionally substituted by halogen; C_{1-4}alkylthio-C_{1-4}alkyl; C_{1-4}alkylsulfonylC_{1-4}alkyl; C_{1-4}alkylsulfonyl; C_{1-4}alkylsulfonyloxy; C_{1-4}alkoxyC_{1-4}alkoxy; $OCH(SR_8)COOR_9$;$NR_{10}R_{11}$; $COOR_{12}$; $C(O)NR_{13}R_{13}'$; $C(O)R_{14}$; R_{15}; $CR_{14}(OC_{1-2}alkyl)_2$ or $CR_{14}(SC_{1-2}alkyl)_2$ whereby the alkyl groups optionally join together to form a ring; $CR_{14}=NOR_{13}$; thienylC_{1-4}alkoxy wherein the thienyl is optionally halo substituted; or C_{1-4}alkoxyC_{1-4}alkoxycarbonyl;

or R_5 and R_6 — join together with the phenyl ring to form a bicyclic ring containing nine to ten ring atoms, one to three of said ring atoms optionally being selected from oxygen, nitrogen and sulfur, and optionally being substituted with one or more groups selected from C_{2-8}alkynyl, halo, oxo, C_{1-4}alkylene-R_{16}, and C_{2-8}alkenyl and C_{1-8}alkyl which is itself optionally substituted by C_{2-5}alkoxycarbonyl, C_{1-4}alkoxy or CN;

R_7 is — H; C_{1-4}alkyl, C_{2-5}alkenyl, C_{2-5}alkynyl, or C_{2-8}cycloalkyl, which hydrocarbyl is unsubstituted or substituted by one or more halo or by CN; cyclopentanonyl; phenyl optionally substituted by O-C_{1-4}alkylene-$COOR_8$; C_{2-5}alkanoyl; C_{2-5}alkoxycarbonyl wherein the alkoxy is optionally substituted by C_{1-4}alkylthio; $C(O)NR_8R_8'$; $C(=NOR_8)COOR_8'$; $P(O)(OR_8)OR_8'$; R_{15}; $C(O)R_{15}$; cyclopentoxycarbonyl; or phenoxy;

R_8 and R_8' — independently are C_{1-4}alkyl;

R_9 is — C_{1-4}alkyl optionally substituted by one or more halo;

R_{10} is — H or C_{1-4}alkyl;

R_{11} is — H; C_{1-4}alkyl, optionally substituted by $P(O)(OR_8)R_8'$; C_{2-5}alkanoyl; C_{2-5}alkoxycarbonyl; or C_{2-5}alkoxycarbonylC_{1-4}-alkyl;

R_{12} is — H; C_{1-10}alkyl; phenyl; an aromatic 5- or 6-membered ring comprising 1 to 3 heteroatoms selected from oxygen, sulphur and nitrogen; $N=C_{2-8}$alkylidene; or C_{1-4}alkyl substituted by one or more groups selected from C_{1-10}alkyl, cycloalkyl, C_{2-10}alkenyl, cycloalkenyl, C_{2-10}alkynyl, $NR_{10}R_{11}$, C_{1-4}alkylthio, CN, phenyl, an aromatic 5- or 6-membered ring comprising 1 to 3 heteroatoms selected from oxygen, sulphur and nitrogen, C_{2-5}alkanoyl, halo, C_{1-4}alkoxy, tri(C_{1-4}alkyl)silyloxy, tri(C_{1-4}alkyl)silyl, C_{2-5}alkoxycarbonyl, $P(O)(OR_8)OR_8'$, C_{2-5}alkanoyloxy, and di(C_{1-4}alkyl)aminocarbonyloxy in which both alkyl groups may be tied together to form a saturated 5 to 6 membered heteroring optionally containing one further heteroatom selected from 0, S and N, and in which any further N-heteroatom present may, depending on the hydrogenation degree of the heteroring, bear a hydrogen or a C_{1-4}alkyl group;

R_{13} is — H or C_{1-4}alkyl; and

R_{13}' is — H, C_{1-4}alkyl, C_{1-4}alkoxy, phenyl, CHO, C_{2-5}alkanoyl, C_{1-4}alkylsulfonyl, C_{2-5}alkoxycarbonylC_{1-4}alkyl or C_{2-5}alkoxycarbonylC_{1-4}alkoxy; or

R_{13} and R_{13}' — together form a 5 to 6 membered heteroring optionally containing one or two further heteroatoms selected from 0, S and N, whereby, depending on the hydrogenation degree of the heteroring, any further N-heteroatom may bear hydrogen or be substituted by C_{1-4}alkyl;

R_{14} is — H or C_{1-4}alkyl;

R_{15} is — a heterocyclic ring having 5 or 6 ring atoms, one to three of said ring atom being selected from oxygen, sulfur and nitrogen, which ring is optionally substituted with one or more groups se-

lected from C_{1-4}alkyl and C_{2-5}alkoxycarbonyl;

R_{16} is — tetrahydropyranyl, 5,6-dihydro-2H-thiinyl, pyridyl, pyrazinyl, oxazolyl, or oxadiazolyl all of which are optionally substituted with C_{1-4}alkyl;

X_1 and X_2 are — independently 0 or S;

k is — 0 or 1; and

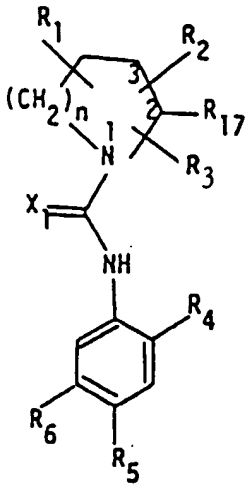
n is — 1 or 2.

2. The compound of formula (I) according to Claim 1 wherein X_2 is oxo, R_1 is H or halo, R_2 is H, R_3 is halo, R_4 is F, R_5 is Cl, CN or Br, and R6 is C_{1-4}alkoxy, C_{2-5}alkynyl, C_{2-5}alkoxycarbonyloxy, C_{2-5}alkoxycarbonyl, C_{2-5}alkoxycarbonylC_{1-4}alkoxy, phenoxyC_{1-4}alkoxy or C_{1-4}alkoxyC_{1-4}alkoxycarbonyl.

3. The compound of formula (I) according to Claim 2 wherein R_1 and R_2 are H, R_3 is halo, R_4 is F, R_5 is halo, cyano or C_{1-4}alkyl, R_6 is C_{1-4}alkoxy, X_1 and X_2 are oxo and n is 2.

4. The compound of formula (I) according to Claim 3 wherein R3 is 7-F, R_5 is Cl, R_6 is isopropyl and m is 1.

5. A compound of the formula (II)



(II)

wherein R_{1-6}, X_1, and n are as defined in Claim 1;

R_{17} is — $C(X_2)OH$; $C(X_2)OW$; COSW; COON=CWW'; $CONHSO_2W$; $CONHOCH_2COOW$; $COOCH_2OCOW$; COOCHWOCOW'; or $CONHOCH_2COOH$;

X_2 is — O or S; and

W and W' are — independently C_{1-8}alkyl, C_{2-8}alkenyl, C_{2-8}alkynyl, or phenyl, each of which is optionally substituted by CN, C_{1-4}alkoxy or one or more halo.

6. A herbicidal composition comprising a compound as defined in Claims 1-5 and an agriculturally acceptable carrier.

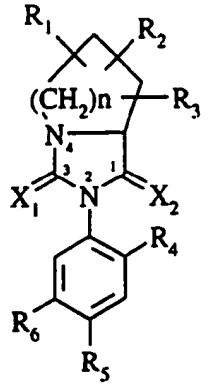
7. A method of combatting weeds which comprises applying to the weeds or their locus a herbicidally effective amount of a compound as defined in Claims 1 to 5.

8. A method of preparing the compound of formula (I) as defined in claim 1 comprising the condensation reaction of

the compound of formula (II) as defined in claim 5.

Patentansprüche

1. Verbindungen der Formel (I)



(I)

worin

R_1 H, ein C_1-C_4-Alkyl-, C_2-C_4-Alkenyl- oder Halogenrest ist;
R_2 H oder Halogen ist;
R_3 Halogen ist;
R_4 H oder Halogen ist;
R_5 Halogen, ein Cyano- oder C_1-C_4-Alkylrest ist;
R_6 Halogen, NO_2, NH_2, CN, ein C_2-C_8-Alkinyl-, C_2-C_8-Alkenyloxy-, C_2-C_8-Alkinyloxy-, $O(C_1$-C_4-Alkylen$)_kR_7$- oder $S(C_1$-C_4-Alkylen$)_kR_7$-Rest ist, die jeweils gegebenenfalls mit CN oder einem oder mehreren Halogenatomen substituiert sind, ein C_1-C_8-Alkylrest, der gegebenenfalls mit einer oder mehreren Gruppen ausgewählt aus Halogen und CN substituiert ist, ein C_2-C_8-Alkenylrest, der gegebenenfalls mit einem oder mehreren Halogenatomen substituiert ist, ein C_2-C_5-Alkoxycarbonyl-C_1-C_4-alkylrest, bei dem das Kohlenstoffatom der Alkylgruppe in α-Stellung zu der Alkoxycarbonylgruppe mit einer oder mehreren C_2-C_5-Alkoxycarbonylgruppen oder einer Cyanogruppe substituiert sein kann, ein C_2-C_5-Alkoxycarbonyloxy-, C_2-C_5-Alkoxycarbonyl-C_1-C_4-alkoxy-C_1-C_4-alkyl-, C_2-C_5-Alkoxycarbonyl-C_2-C_5-alkenylrest, bei dem die Alkenylgruppe gegebenenfalls mit Halogen substituiert ist, ein C_1-C_4-Alkylthio-C_1-C_4-alkyl-, C_1-C_4-Alkylsulfonyl-C_1-C_4-alkyl-, C_1-C_4-Alkylsulfonyl-, C_1-C_4-Alkylsulfonyloxy-, C_1-C_4-Alkoxy-C_1-C_4-alkoxyrest, $OCH(SR_8)COOR_9$, $NR_{10}R_{11}$, $COOR_{12}$, $C(O)NR_{13}R_{13'}$, $C(O)R_{14}$, R_{15}, $CR_{14}(OC_1$-C_2alkyl$)_2$ oder $CR_{14}(SC_{1\text{-}2}$alkyl$)_2$, worin die Alkylgruppen gegebenenfalls miteinander einen Ring bilden, $CR_14{=}NOR_{13}$, ein ThienylC_1-C_4-alkoxyrest, bei dem der Thienylrest gegebenenfalls mit Halogen substituiert ist oder ein C_1-C_4-Alkoxy-C_1-C_4-alkoxycarbonylrest ist; oder
R_5 und R_6 zusammen mit dem Phenylring einen bicyclischen Ring bilden, der 9 bis 10 Ringatome enthält, wovon 1 bis 3 Ringatome gegebenenfalls ausgewählt sind aus Sauerstoff, Stickstoff und Schwefel und der gegebenenfalls mit einer oder mehreren Gruppen ausgewählt aus C_2-C_8-Alkinyl-, Halogen-, Oxo-, C_1-C_4-Alkylen-R_{16}- und C_2-C_8-Alkenyl- und C_1-C_8-Alkylresten substituiert sein kann, die wiederum mit C2-C5-Alkoxycarbonyl-, C_1-C_4-Alkoxy- oder CN-Resten substituiert sein können,
R_7 H, ein C_1-C_4-Alkyl-, C_2-C_5-Alkenyl-, C_2-C_5-Alkinyl- oder C_3-C_8-Cycloalkylrest, wobei der Kohlenwasserstoffrest mit einem oder mehreren Halogenatomen oder CN substituiert ist oder unsubstituiert ist; ein Cyclopentanonylrest; ein Phenylrest, der gegebenenfalls mit O-C_1-C_4-Alkylen-$COOR_8$-Resten substituiert ist, ein C_2-C_5-Alkanoylrest, ein C_2-C_5-Alkoxycarbonylrest, bei dem der Alkoxyrest gegebenenfalls mit C_1-C4-Alkylthio substituiert ist, $C(O)NR_8R_{8'}$, $C(=NOR_8)COOR_{8'}$, $P(O)(OR_8)OR_{8'}$, R_{15}, $C(O)R_{15}$, ein Cyclopentoxycarbonylrest oder ein Phenoxyrest ist;
R_8 und $R_{8'}$unabhängig C_1-C_4-Alkylreste sind;
R_9 ein C_1-C_4-Alkylrest ist, der gegebenenfalls mit einem oder mehreren Halogenatomen substituiert ist;
R_{10} H oder ein C_1-C_4-Alkylrest ist;
R_{11} H, ein C_1-C_4-Alkylrest, der gegebenenfalls mit $P(O)(OR_8)R_{8'}$ substituiert ist, ein C_2-C_5-Alkanoyl-, C_2-C_5-

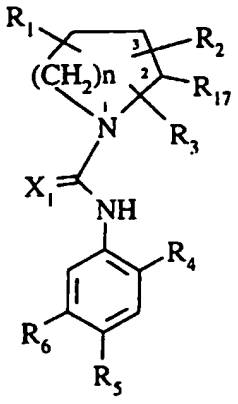
Alkoxycarbonyl- oder C_2-C_5-Alkoxycarbonyl-C_1-C_4-alkylrest ist;
R_{12} H, ein C_1-C_{10}-Alkylrest, Phenylrest, ein aromatischer 5- oder 6-gliedriger Ring mit 1 bis 3 Heteroatomen ausgewählt aus Sauerstoff, Schwefel und Stickstoff, ein N=C_2-C_8-Alkylidenrest oder ein C_1-C_4-Alkylrest ist, der mit einer oder mehreren Gruppen substituiert ist ausgewählt aus C_1-C_{10}-Alkyl-, Cycloalkyl-, C_2-C_{10}Alkenyl-, Cycloalkenyl-, C_2-C_{10}-Alkinyl-, $NR_{10}R_{11}$-, C_1-C_4-Alkylthio-, CN-, Phenylresten, einem aromatischen 5- oder 6-gliedrigen Ring mit 1 bis 3 Heteroatomen ausgewählt aus Sauerstoff, Schwefel und Stickstoff, C_2-C_5-Alkanoyl-, Halogen-, C_1-C_4-Alkoxy-, Tri(C_1-C_4-alkyl)silyloxy-, Tri(C_1-C_4-alkyl)silyl-, C_2-C_5-Alkoxycarbonyl-, $P(O)(OR_8)OR_8$-, C_2-C_5-Alkanoyloxyresten und einem Di(C_1-C_4-alkyl)aminocarbonyloxyrest substituiert ist, bei dem beide Alkylgruppen miteinander verbunden sein können unter Bildung eines gesättigten 5- bis 6-gliedrigen Heterorings, der gegebenenfalls ein weiteres Heteroatom ausgewählt aus O, S und N enthält, und worin jedes weitere vorhandene N-Heteroatom abhängig von dem Hydrierungsgrad des Heterorings ein Wasserstoffatom oder eine C_1-C_4-Alkylgruppe tragen kann;
R_{13} H oder ein C_1-C_4-Alkylrest ist und
$R_{13'}$ H, ein C_1-C_4-Alkyl-, C_1-C_4-Alkoxy-, Phenyl-, CHO-, C_2-C_5-Alkanoyl-, C_1-C_4-Alkylsulfonyl-, C_2-C_5-Alkoxycarbonyl-C_1-C_4-alkyl- oder C_2-C_5-Alkoxycarbonyl-C_1-C_4-alkoxyrest ist oder
R_{13} und $R_{13'}$ zusammen einen 5- bis 6-gliedrigen Heteroring bilden, der gegebenenfalls 1 oder 2 weitere Heteroatome ausgewählt aus O, S und N enthält, wobei abhängig vom Hydrierungsgrad des Heterorings jedes weitere N-Heteroatom Wasserstoffatome tragen kann oder mit C_1-C_4-Alkyl substituiert sein kann;
R_{14} H oder ein C_1-C_4-Alkylrest ist;
R_{15} ein heterocyclischer Ring mit 5 oder 6 Ringatomen ist, wobei 1 bis 3 Ringatome ausgewählt sind aus Sauerstoff, Schwefel und Stickstoff, wobei der Ring gegebenenfalls mit einer oder mehreren Gruppen ausgewählt aus C_1-C_4-Alkyl- und C_2-C_5-Alkoxycarbonylresten substituiert ist;
R_{16} ein Tetrahydropyranyl-, 5,6-Dihydro-2H-thiinyl-, Pyridyl-, Pyrazinyl-, Oxazolyl- oder Oxadiazolylrest ist, die jeweils gegebenenfalls mit C_1-C_4-Alkyl substituiert sind;
X_1 und X_2unabhängig O oder S sind;
k 0 oder ist und
n 1 oder 2 ist.

2. Verbindung der Formel (I) nach Anspruch 1, worin X_2 ein Oxorest ist, R_1 H oder Halogen ist, R_2 H ist, R_3 Halogen ist, R_4 F ist, R_5 Cl, CN oder Br ist und R_6 ein C_1-C_4-Alkoxy-, C_2-C_5-Alkinyl-, C_2-C_5-Alkoxycarbonyloxy-, C_2-C_5-Alkoxycarbonyl-, C_2-C_5-Alkoxycarbonyl-C_1-C_4-alkoxy-, Phenoxy-C_1-C_4-alkoxy- oder C_1-C_4-Alkoxy-C_1-C_4-alkoxycarbonylrest ist.

3. Verbindung der Formel (I) nach Anspruch 2, worin R_1 und R_2 H sind, R_3 Halogen ist, R_4 F ist, R_5 ein Halogen-, Cyano- oder C_1-C_4-Alkylrest ist, R_6 ein C_1-C_4-Alkoxyrest ist, X_1 und X_2 Oxoreste sind und n 2 ist.

4. Verbindung der Formel (I) nach Anspruch 3, worin R_3 7-F ist, R_5 Cl ist, R_6 ein Isopropylrest ist und m l ist.

5. Verbindung der Formel (II)



(II)

worin

R_{1-6}, X_1 und n wie in Anspruch 1 definiert sind;
R_{17} $C(X_2)OH$, $C(X_2)OW$, COSW, $COON{=}CWW'$, $CONHSO_2W$, $CONHOCH_2COOW$, $COOCH_2OCOW$, $COOCHWOCOW'$ oder $CONHOCH_2COOH$ ist,
X_2 O oder S ist und
W und W' unabhängig C_1-C_8-Alkyl-, C_2-C_8-Alkenyl-, C_2-C_8-Alkinyl- oder Phenylreste sind, die jeweils gegebenenfalls mit CN, C_1-C_4-Alkoxy oder einem oder mehreren Halogenatomen substituiert sind.

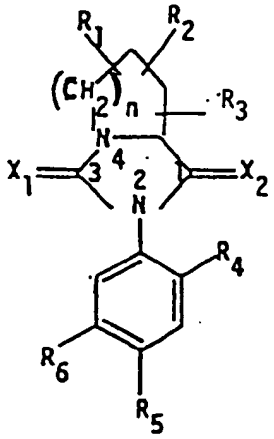
6. Herbizidzusammensetzung umfassend eine Verbindung wie in einem der Ansprüche 1 bis 5 definiert und einen landwirtschaftlich annehmbaren Träger.

7. Verfahren zur Bekämpfung von Unkräutern, welches das Ausbringen einer herbizid wirksamen Menge einer Verbindung nach Anspruch 1 bis 5 auf die Unkräuter oder deren Standort umfasst.

8. Verfahren zur Herstellung der Verbindung der Formel (I), wie in Anspruch 1 definiert, umfassend die Kondensationsreaktion der Verbindung der Formel (II), wie in Anspruch 5 definiert.

Revendications

1. Un composé de formule (I)



(I)

dans laquelle

R_1 signifie H, un groupe alkyle en C_1-C_4, alcényle en C_2-C_4 ou un halogène;

R_2 signifie H ou un halogène,

R_3 signifie un halogène,

R_4 signifie H ou un halogène,

R_5 signifie un halogène ou un groupe cyano ou alkyle en C_1-C_4;

R_6 signifie un halogène: NO_2; NH_2; CN; alcynyle en C_2-C_8; alcényloxy en C_2-C_8; alcynyloxy en C_2-C_8; O(alkylène en C_1-C_4)$_k$$R_7$, ou S(alkylène en C_1-C_4)$_k$$R_7$, chacun d'entre eux est éventuellement substitué par CN ou par un ou plusieurs halogènes; alkyle en C_1-C_8 éventuellement substitué par 1 ou plusieurs groupes choisis parmi un halogène et CN; alcényle en C_2-C_8 éventuellement substitué par un ou plusieurs halogènes; (alcoxycarbonyl en C_2-C_8)alkyle en C_1-C_4, où l'atome de carbone du groupe alkyle en position alpha par rapport

au groupe alcoxycarbonyle peut être substitué par un groupe alcoxycarbonyle en C_2-C_5 supplémentaire ou un groupe cyano;
alcoxycarbonyloxy en C_2-C_5; (alcoxycarbonyl en C_2-C_5)(alcoxy en C_1-C_4)alkyle en C_1-C_4; (alcoxycarbonyl en C_2-C_5)alcényle en C_2-C_5, où le groupe alcényle est éventuellement substitué par de l'halogène; (alkylthio en C_1-C_4)alkyle en C_1-C_4; (alkylsulfonyl en C_1-C_4)alkyle en C_1-C_4;
alkylsulfonyle en C_1-C_4; alkylsulfonyloxy en C_1-C_4; (alcoxy en C_1-C_4)alcoxy en C_1-C_4; $OCH(SR_8)COOR_9$; $NR_{10}R_{11}$; $COOR_{12}$; $C(O)NR_{13}R_{13}'$; $C(O)R_{14}$; R_{15}; CR_{14}(O-alkyle en C_1-C_2)$_2$ ou CR_{14}(S-alkyle en C_1-C_2)$_2$ où les groupes alkyle s'unissent éventuellement pour former un cycle;
CR_{14}=NOR_{13}; thiénylalcoxy en C_1-C_4 où le groupe thiényle est éventuellement substitué par de l'halogène; ou (alcoxy en C_1-C_4)alcoxycarbonyle en C_1-C_4;

ou bien R_5 et R_6 — s'unissent au cycle phényle pour former un cycle bicyclique contenant de 9 à 10 atomes dans le cycle, 1 à 3 desdits atomes dans le cycle étant éventuellement choisis parmi l'oxygène, l'azote et le soufre, et étant éventuellement substitués par 1 ou plusieurs groupes choisis parmi un groupe alcynyle en C_2-C_8, un halogène, oxo, (alkylène en C_1-C_4)R_{16}, et alcényle en C_2-C_8 et alkyle en C_1-C_8 qui est lui-même éventuellement substitué par un groupe alcoxycarbonyle en C_2-C_5, alcoxy en C_1-C_4 ou CN;

R_7 — signifie H; alkyle en C_1-C_4, alcényle en C_2-C_5, alcynyle en C_2-C_5 ou cycloalkyle en C_3-C_8, dont le groupe hydrocarboné est non substitué ou substitué par un ou plusieurs halogènes ou par CN; cyclopentanonyle; phényle éventuellement substitué par un groupe O-(alkylène en C_1-C_4)-$COOR_8$; alcanoyle en C_2-C_5; alcoxycarbonyle en C_2-C_5 où le groupe alcoxy est éventuellement substitué par un groupe alkylthio en C_1-C_4; $C(O)NR_8R_8'$; $C(=NOR_8)COOR_8'$; $P(O)(OR_8)OR_8'$; R_{15}; $C(O)R_{15}$; cyclopentoxycarbonyle; ou phénoxy;

R_8 et R_8' — signifient indépendamment un groupe alkyle en C_1-C_4;

R_9 — signifie un groupe alkyle en C_1-C_4 éventuellement substitué par un ou plusieurs halogènes;

R_{10} — signifie H ou un groupe alkyle en C_1-C_4;

R_{11} — signifie H; alkyle en C_1-C_4, éventuellement substitué par $P(O)(OR_8)R_8'$; alcanoyle en C_2-C_5; alcoxycarbonyle en C_2-C_5; ou (alcoxycarbonyl en C_2-C_5)alkyle en C_1-C_4;

R_{12} — signifie H; alkyle en C_1-C_{10}; phényle; un cycle aromatique à 5 ou 6 chaînons comprenant de 1 à 3 hétéroatomes choisis parmi l'oxygène, le soufre et l'azote; N=alkylidène en C_2-C_8; ou alkyle en C_1-C_4 substitué par un ou plusieurs groupes choisis parmi un groupe alkyle en C_1-C_{10}, cycloalkyle, alcényle en C_2-C_{10}, cycloalcényle, alcynyle en C_2-C_{10}, $NR_{10}R_{11}$, alkylthio en C_1-C_4, CN, phényle, un cycle aromatique à 5 ou 6 chaînons comprenant de 1 à 3 hétéroatomes choisis parmi l'oxygène, le soufre et l'azote, alcanoyle en C_2-C_5, un halogène, alcoxy en C_1-C_4, tri(alkyl en C_1-C_4)silyloxy, tri(alkyl en C_1-C_4)silyle, alcoxycarbonyle en C_2-C_5, $P(O)(OR_8)OR_8'$, alcanoyloxy en C_2-C_5 et di(alkyl en C_1-C_4)aminocarbonyloxy où les deux groupes alkyle peuvent être liés ensemble pour former un hétérocycle saturé à 5 ou 6 chaînons contenant éventuellement un autre hétéroatome choisi parmi O, S et N, et où tout autre N-hétéroatome présent peut, en fonction du degré d'hydrogénation de l'hétérocycle, porter un hydrogène ou un groupe alkyle en C_1-C_4;

R_{13} — signifie H ou un groupe alkyle en C_1-C_4, et

R_{13}' — signifie H, alkyle en C_1-C_4, alcoxy en C_1-C_4, phényle, CHO, alcanoyle en C_2-C_5, alkylsulfonyle en C_1-C_4, (alcoxycarbonyl en C_2-C_5)alkyle en C_1-C_4 ou (alcoxycarbonyl en C_2-C_5) alcoxy en C_1-C_4; ou bien

R_{13} et R_{13}' — forment ensemble un hétérocycle à 5 ou 6 chaînons contenant éventuellement un ou deux autres hétéroatomes choisis parmi O, S et N, où, en fonction du degré d'hydrogénation de l'hétérocycle, tout autre N-hétéroatome peut porter un hydrogène ou être substitué par un

groupe alkyle en C_1-C_4;

R_{14} signifie H ou un groupe alkyle en C_1-C_4;

R_{15} signifie un hétérocycle ayant 5 ou 6 atomes dans le cycle, 1 à 3 desdits atomes dans le cycle étant choisis parmi l'oxygène, le soufre et l'azote, ledit cycle est éventuellement substitué par un ou plusieurs groupes choisis parmi un groupe alkyle en C_1-C_4 et alcoxycarbonyle en C_2-C_5;

R_{16} signifie un groupe tétrahydropyranyle, 5,6-dihydro-2H-thiényle, pyridyle, pyrazinyle, oxazolyle ou oxadiazolyle, tous étant éventuellement substitués par un groupe alkyle en C_1-C_4;

X_1 et X_2 signifient indépendamment O ou S;

k signifie 0 ou 1; et

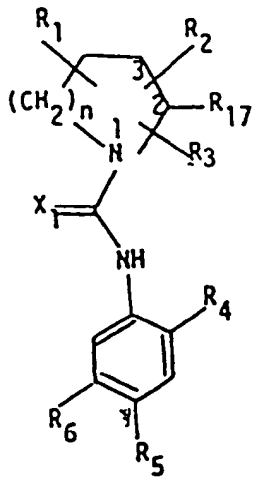
n signifie 1 ou 2.

2. Le composé de formule (I) selon la revendication 1, dans lequel X_2 signifie oxo, R_1 signifie H ou un halogène, R2 signifie H, R3 signifie un halogène, R4 signifie F, R_5 signifie Cl, CN ou Br, et R_6 signifie un groupe alcoxy en C_1-C_4, alcynyle en C_2-C_5, alcoxycarbonyloxy en C_2-C_5, alcoxycarbonyle en C_2-C_5, (alcoxycarbonyl en C_2-C_5)alcoxy en C_1-C_4, phénoxyalcoxy en C_1-C_4 ou (alcoxy en C_1-C_4)alcoxycarbonyle en C_1-C_4.

3. Le composé de formule (I) selon la revendication 2, dans lequel R_1 et R_2 signifient H, R_3 signifie un halogène, R_4 signifie F, R_5 signifie un halogène, un groupe cyano ou alkyle en C_1-C_4, R_6 signifie un groupe alcoxy en C_1-C_4, X_1 et X_2 signifient un groupe oxo et n signifie 2.

4. Le composé de formule (I) selon la revendication 3, dans lequel R_3 signifie 7-F, R_5 signifie Cl, R_6 signifie isopropyle et m signifie 1.

5. Un composé de formule (II)



(II)

où $R_{1\text{-}6}$, X_1, et n sont tels que définis à la revendication 1;

R_{17} signifie $C(X_2)OH$; $C(X_2)OW$;COSW;COON=CWW';$CONHSO_2W$; $CONHOCH_2COOW$; $COOCH_2OCOW$; COOCHWOCOW'; ou $CONHOCH_2COOH$;

X_2 signifie O ou S; et

W et W' signifient indépendamment un groupe alkyle en C_1-C_8, alcényle en C_2-C_8, alcynyle en C_2-C_8 ou phényle, chacun d'entre eux est éventuellement substitué par CN, un groupe alcoxy en C_1-C_4 ou un ou plusieurs halogènes.

6. Une composition herbicide comprenant un composé tel que défini aux revendications 1-5 et un véhicule acceptable en agriculture.

7. Une méthode de lutte contre les mauvaises herbes qui comprend l'application aux mauvaises herbes ou à leur lieu de croissance d'une quantité efficace du point de vue herbicide d'un composé tel que défini aux revendications 1 à 5.

8. Une méthode de préparation du composé de formule (I) tel que défini à la revendication 1, selon laquelle on condense le composé de formule (II) tel que défini à la revendication 5.